Self-consistent diffusion coefficients in nearly-one-dimensional paramagnets

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Self-consistent diffusion coefficients in nearly-one-dimensional paramagnets*

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We calculate the off-chain diffusion coefficients in nearly-one-dimensional paramagnets self-consistently. The problem is solved by using a simplified mode-coupling theory. The results can be used to interpret the electron-paramagnetic-resonance linewidth in these systems.

Magnetic resonance has proven to be a very powerful technique to study the relaxation dynamics of paramagnets. In particular, the one-dimensional magnets can be studied well in this way. The slow $k \approx 0$ modes determine the EPR spectrum of a one-dimensional Heisenberg magnet entirely.[1-4] Richards and Salamon[5] have shown that also in the case of a two-dimensional magnet the long-wavelength modes have a dominating influence on the ESR spectrum. The relative weight of the $k \approx 0$ modes in a three-dimensional magnet can be neglected and all the modes contribute. The one dimensionality of a Heisenberg magnet is determined by the ratio of the interchain exchange and intrachain exchange constants. Actually, the one dimensionality of a paramagnet, as far as magnetic resonance is concerned, is determined by the ratio of the off-chain and intrachain diffusion constants. Hennessy, McElwee, and Richards[6] were the first to show that off-chain relaxation is faster than one would expect on the basis of a simple calculation based on moments. However, the off-chain spin motion was calculated with a Kubo and Tomita-type theory[7] and turned out to be nondiffusive. Reiter[8] has indicated that the calculation should be done self-consistently, and he showed that in that case the off-chain spin motion was diffusive. His numerical calculation was questioned because of the many approximations that were made.[9] From this it can be concluded that more reliable off-chain diffusion coefficients are needed.

We have calculated off-chain diffusion coefficients self-consistently for two cases: (i) a two-dimensional lattice; and (ii) a simple tetragonal lattice. These two models are of most interest from an experimental point of view. The calculation uses the Mori projection operator technique.[10] The self-energy $\Gamma(\vec{k}, z)$ is defined as the one-sided Fourier transform of the memory function $\Gamma(\vec{k}, t)$, which is defined by

$$\dot{\sum}(\vec{k}, t) = -\int_0^t \Gamma(\vec{k}, t-\tau) \sum(\vec{k}, \tau)\, d\tau \,, \qquad (1)$$

where

$$\sum(\vec{k}, t) = \langle S^z(\vec{k}, t) S^z(-\vec{k}) \rangle \,. \qquad (2)$$

The time dependence of $\Gamma(\vec{k}, t)$ is determined by a modified Liouville operator

$$\mathcal{L}' = (1-P)\mathcal{L}(1-P) \equiv Q\mathcal{L}Q \,, \qquad (3)$$

where $\mathcal{L}$ is the Liouville operator of the Heisenberg Hamiltonian, and in which the Mori projection operator P is defined by

$$PX = \sum_{\vec{k}} S^z(\vec{k}) \langle S^z(\vec{k}) S^z(-\vec{k}) \rangle^{-1} (S^z(\vec{k}) \mid X) \,, \qquad (4)$$

in which the scalar product is defined by $(A \mid B) = \langle A^\dagger B \rangle$ and where X is an arbitrary operator. If the equation of motion of $\sum(\vec{k}, t)$ is a diffusion equation for long times and long wavelengths, then

$$\lim_{k \to 0, z \to 0} \Gamma(\vec{k}, z) = D_1 k_x^2 + D_2 k_y^2 + D_3 k_z^2 \,. \qquad (5)$$

We have already limited ourselves here to lattices which do not allow cross terms to occur in Eq. (5). The formal expression for the self-energy is

$$\Gamma(\vec{k}, z) = i (Q\mathcal{L}S^z(\vec{k}) \| [z - \mathcal{L}']^{-1} Q\mathcal{L}S^z(\vec{k})) \times \langle S^z(\vec{k}) S^z(-\vec{k}) \rangle^{-1} \,. \qquad (6)$$

If one wants to calculate $\Gamma(\vec{k}, z)$ from Eq. (6), one has to know the combination of four-spin correlation functions which occurs there. At this point we need an approximation for the self-energy. The most popular approximation is to neglect the operator P and to decouple the correlation functions simultaneously. This approximation is known as the independent mode approximation (IMA) and the resulting equations of motion are the mode-coupling form.[11] This approach seems somewhat arbitrary although it can be given a solid basis in terms of diagrammatic expansions.[12] It is possible to construct diagrams which give all the moments correct to order c^{-1}, c being the number of nearest neighbors. The lowest-order result, which is a partial summation of these diagrams (the bubble approximation), is equivalent to the mode-coupling theories.

At first sight one could think of alternative simplifications, for instance to neglect P without de-

coupling. However, we will demonstrate that this leads to unphysical results. Using $Q\mathcal{L}S^z(\vec{k}) = \mathcal{L}S^z(\vec{k})$ for a paramagnet and neglecting P in the propagator of Eq. (6) results in

$$\Gamma(\vec{k},z) = i\,(\mathcal{L}S^z(\vec{k})\,|(z-\mathcal{L})^{-1}\mathcal{L}S^z(\vec{k}))\times\langle S^z(\vec{k})S^z(-\vec{k})\rangle^{-1}. \tag{7}$$

Equation (7) can be solved readily. Introducing the operator identity

$$\mathcal{L}(z-\mathcal{L})^{-1}\mathcal{L} = z^2(z-\mathcal{L})^{-1} - \mathcal{L} - z$$

in Eq. (7) gives

$$\Gamma(\vec{k},z) = \frac{iz^2(S^z(\vec{k})\,|(z-\mathcal{L})^{-1}S^z(\vec{k}))}{\langle S^z(\vec{k})S^z(-\vec{k})\rangle} - iz\,. \tag{8}$$

Using the one-sided Fourier transform of Eq. (1), one obtains

$$\Gamma(\vec{k},z) = i\{z^2/[z+i\Gamma(\vec{k},z)] - z\}\,. \tag{9}$$

This has the unacceptable effect that $\Gamma(\vec{k},z) = 0$, independent of $\vec{k}$. Retaining P in the decoupled function is obviously wrong since this would prevent the two-spin correlation functions from decaying.

The conclusion is that the mode-coupling approach is one of the simplest nontrivial descriptions of spin dynamics. Within this approach the expression for the self-energy in the high-temperature limit becomes

$$\Gamma(\vec{k},z) = [\tfrac{1}{3}S(S+1)]^{-1}\sum_{\vec{k}'}[J(\vec{k}-\vec{k}') - J(\vec{k}')]^2\int_0^\infty e^{izt}\langle S^z(\vec{k}',t)S^z(-\vec{k}')\rangle\langle S^z(\vec{k}-\vec{k}',t)S^z(\vec{k}'-\vec{k})\rangle\,dt\,, \tag{10}$$

where $J(\vec{k})$ is the spatial transform of $J(r_{ij})$, the exchange interaction. Rather than solving Eq. (10) numerically exactly for anisotropic lattices, which is a formidable task, we will solve Eq. (10) approximately. Later on we will compare our results, where possible, with the full mode-coupling approach. We will assume that the two-spin correlation functions have a certain analytic form. As only adjustable parameters we introduce the three diffusion coefficients D_1, D_2, and D_3. The limit

$$\lim_{k\to 0,\,z\to 0}\Gamma(\vec{k},z)$$

can be calculated using Eq. (10), and since this limit is known [See Eq. (5)] self-consistent equations for the diffusion constants are acquired. The form we choose to be appropriate for the high-temperature two-spin correlation functions is

$$\langle S^z(\vec{k},t)S^z(-\vec{k})\rangle = \tfrac{1}{3}S(S+1)\exp[(-D_1\sin^2\tfrac{1}{2}k_xa - D_2\sin^2\tfrac{1}{2}k_yb - D_3\sin^2\tfrac{1}{2}k_zc)4t]\,. \tag{11}$$

First of all, we note that the expression has the correct behavior of spin diffusion for long terms and long wavelengths. The kinetic approach of Reiter[13] indicates that the simplest approximation for the self-energy which has the correct small-frequency behavior, is the supposition that the self-energy is proportional to the second moment. This is tantamount to assuming expression (11) to be valid. In addition, we want to point out that expression (11) can be obtained from a random walk picture of the dynamics. The most important aspect of assuming expression (11) is the fact that the diffusion constants can be calculated relatively simple. The self-consistent equations to be solved for a tetragonal lattice, with only nearest-neighbor exchange interaction, are

$$\frac{3D_1^2}{a^4} = S(S+1)J_1^2\int_0^\infty I_1(x)I_0^2(px)\times x^{-1}\exp[-x(1+2p)]\,dx\,, \tag{12a}$$

and

$$\frac{3pD_1D_2}{a^2b^2} = S(S+1)J_2^2\int_0^\infty I_1(px)I_0(px)I_0(x)\times x^{-1}\exp[-x(1+2p)]\,dx\,, \tag{12b}$$

where p is defined as D_2a^2/D_1b^2, a measure for the one dimensionality of the diffusion process, J_1 is the exchange interaction along the chain, J_2 is the exchange constant perpendicular to the chain, and $I_n(\alpha)$ is the modified Bessel function of argument α and order n.[14] It is straightforward to derive the appropriate equations for the two-dimensional lattice from Eqs. (12a) and (12b). Equations (12a) and (12b) have been solved numerically. The major parts of the integrals were computed by analytic integration of expansions of the Bessel functions. The results are presented in Fig. 1.

Before we discuss the possible applications of these diffusion coefficients we would like to com-

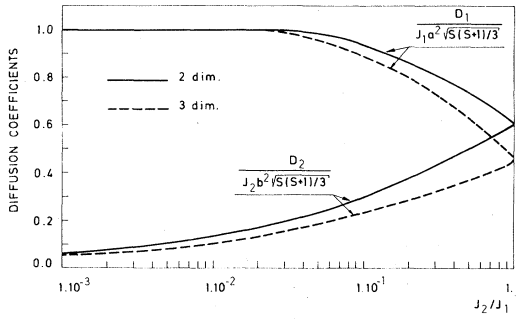

FIG. 1. Diffusion coefficients in anisotropic paramagnets as a function of J_2/J_1. J_2 is the off-chain exchange interaction.

ment on the validity of our calculation with respect to the full mode-coupling approach. The assumption expressed in Eq. (11) describes only the long-time and long-wavelength behavior correctly. We expect the largest difference between our result and the full mode-coupling approach to show up for three-dimensional lattices and the smallest difference for one-dimensional lattices. In one-dimensional wave-vector sums the relative weight of the $k \approx 0$ region is large and for these wave vectors Eq. (11) is a good approximation. In three-dimensional wave-vector sums all modes contribute whereas Eq. (11) only describes the long wavelengths correctly. Our value for the diffusion coefficient in the case of the three-dimensional simple cubic lattice is $0.26\, Ja^2\, [S(S+1)]^{1/2}$. The numerical factor in the full mode-coupling theory is 0.33,[15] which differs by $\approx 20\%$. We calculate the diffusion coefficient for a square lattice to be $0.34\, Ja^2\, [S(S+1)]^{1/2}$. To our knowledge, there is no full mode-coupling solution for the square lattice. Morita[16] finds $0.46\, Ja^2\, [S(S+1)]^{1/2}$ using a stochastic assumption about the memory function.

The full mode-coupling diffusion coefficient in one dimension is $1.39\, Ja^2\, [S(S+1)]^{1/2}$,[17] and our result is $0.58\, Ja^2\, [S(S+1)]^{1/2}$, which is surprising. However, a check on the full mode-coupling calculation of the diffusion coefficient in one-dimensional paramagnets[17] shows that the original number $0.69\, Ja^2\, [S(S+1)]^{1/2}$ is correct. This clarifies the situation considerably because this differs from our result less than 20%. It also shows that the two-spin correlation functions obtained with the mode-coupling theory are not as good as has been claimed because the value of the diffusion coefficient found with computer simulation of one-dimensional spin dynamics is $1.32\, Ja^2 S$.[18] We conclude that our results differ less than 20% from the full mode-coupling solution which is very gratifying. In the first place, because the mode-coupling equations are not more accurate anyway, and in the second place, our calculation is much simpler. There is no reason to prefer perturbation-type calculations for off-chain motion,[6] which give unphysical nondiffusive motion, to the mode-coupling approach. We claim that anisotropic diffusion equations with the here-presented off-chain diffusion coefficients are the most reliable descriptions of long-time off-chain motion in nearly one-dimensional Heisenberg magnets up to date. Before we turn to the possible applications of the off-chain diffusion coefficients, we will compare our results with the results of Reiter.[8] Our calculations are valid in the complete range of p, up to $p = 1$, and, in fact, they are the first calculations which cover this range. To what extent the off-chain diffusion influences the on-chain diffusion was not known before. In the range $0.001 < J_2/J_1 < 0.05$ the equation $D_2 = 0.51\, (J_2/J_1)^{1/3}\, J_2[\frac{1}{3}S(S+1)]^{1/2}$ gives a reasonable fit to the results for the tetragonal lattice, and in the same range the equation $D_2 = 0.66\, (J_2/J_1)^{1/3}\, J_2[\frac{1}{3}S(S+1)]^{1/2}$ gives a reasonable fit to the results for the two-dimensional lattice. Reiter's result is $D_2 = 1.12\, (J_2/J_1)^{1/3} \times J_2[\frac{1}{3}S(S+1)]^{1/2}$ for the three-dimensional case and the two-dimensional case has not been calculated before. In the indicated range of J_2/J_1, the difference in D_2 in the tetragonal lattice is not dramatic, but, as has been indicated, our results have a firmer basis and are valid outside the indicated range of J_2/J_1. The diffusion coefficients calculated here are particularly useful for the EPR absorption in paramagnets. The most direct application is to the case of magnetically inequivalent chains. These chains have different resonance frequencies, and the magnitude of the interchain coupling determines whether or not an exchange averaged spectrum is observed. If an exchange narrowed spectrum is observed, then the linewidth depends in a very simple way on the off-chain diffusion coefficients.[9] For treating equivalent chains with interchain interactions one has to use the off-chain diffusion coefficients in an ESR theory. For this one can use the Kubo and Tomita theory[7] or the theory of Reiter and Boucher.[2] In both cases numerical evaluation will be necessary. This is beyond the scope of the present paper since this is only worthwhile doing if one wants to explain the ESR characteristics of a specific compound.

We have presented in this paper the calculation of off-chain diffusion coefficients in nearly-one-dimensional Heisenberg magnets. The method which has been used is a simplified version of the mode-coupling approach, and the difference with the full mode-coupling approach is estimated to be less than 20%. The main application of the diffusion coefficients will be the calculations of the ESR linewidth in nearly-one-dimensional Heisenberg magnets.

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